Desalination options for high TDS oil and gas produced water

24th Annual Produced Water Society Seminar

Prakash Narayan Govindan
Chief Technology Officer
Gradiant Corporation
govindan@gradiantcorp.com

January 16th, 2014

Produced water can be the most challenging feed for desalination

What is in the water?

1. Dispersed oil ("Oil & Grease")
   - Droplets <10 µm interfere with treatment/ processing operations
2. Soluble Organic components
   - PAHs (e.g. naphthalene), VOCs (e.g. BTEX), Organic acids, Phenols
3. Artificially added chemicals
   - Biocides, corrosion inhibitors, friction reducers
   - Affect water properties and oil/water separation; mainly concerns flowback
4. Total suspended solids (TSS)
   - Sand/silt, clay, proppant etc.
5. Microbiological contamination
6. Dissolved content(TDS)
   - Monovalent ions (Na, K, Cl, Br, etc.), Divalent ions (Ca, Mg, Ba, Sr, SO4, CO3 etc.)
   - NORM (Ra-226, Ra-228)
   - Generally most expensive and complicated to remove

Volatiles Data (µg/L)
Isopropylbenzene
Acetone
Naphthalene
1, 3, 5 - Trimethylbenzene
1, 2, 4 - Trimethylbenzene
Xylenes (total)
Benzene
Ethylbenzene
Toluene

Typical VOCs
Source: Hayes, GTI

Fracturing proppant
Source: momentive.com

GRADIANT CORPORATION

Feed quality highly variable; TDS can be as high as >200k ppm

Constituent	Units	Shale gas, Marcellus	Unconventional oil, Permian
Bromide	mg/L	1678	2960
Chloride	**mg/L**	**115194**	**62200**
Hardness	**mg/L CaCO3**	**51037**	**7410**
Oil & grease	**mg/L**	**615**	**8**
BOD	mg/L	525	8
COD	mg/L	46818	3160
pH	Std. Units	6.27	7.01
Phenolics	mg/L	0.125	ND
TDS @ 180 C	**mg/L**	**211,406**	**125,000**
TSS	mg/L	2461	418
Sulfate	mg/L	26	353
Surfactants	mg/L	1.22	0.37
Barium	mg/L	8923	4
Calcium	mg/L	13875	2290
Iron	mg/L	128	ND
Magnesium	mg/L	1216	412
Sodium	**mg/L**	**46695**	**29900**
Strontium	mg/L	4064	615

Representative samples from Marcellus shale gas wells and Permian unconventional oil wells
Source: Gradiant Corp. field testing

Need for desalination can be driven by different variables

PA: Stringent discharge limits and high cost of disposal

Constituent	Limit
Aluminum	0.2 mg/L
Ammonia	2 mg/L
Arsenic	10 µg/L
Barium	2 mg/L
Benzene	0.12 µg/L
Beryllium	4 µg/L
Boron	1.6 mg/L
Bromide	0.1 mg/L
Butoxyethanol	0.7 mg/L
Cadmium	0.16 µg/L
Chloride	25 mg/L
COD	15 mg/L
Chromium	10 µg/L
Copper	5 µg/L
Ethylene Glycol	13 µg/L
Gross Alpha	15 pCi/L
Gross Beta	1,000 pCi/L
Iron	0.3 mg/L
Lead	1.3 µg/L

Constituent	Limit
Magnesium	10 mg/L
Manganese	0.2 mg/L
MBAS (Surfactants)	0.5 mg/L
Methanol	3.5 mg/L
Molybdenum	0.21 mg/L
Nickel	30 µg/L
Nitrite-Nitrate Nitrogen	2 mg/L
Oil & Grease	ND
pH	6.5-8.5 SU
Radium-226 + Radium-228	5 pCi/L (combined)
Selenium	4.6 µg/L
Silver	1.2 µg/L
Sodium	25 mg/L
Strontium	4.2 mg/L
Sulfate	25 mg/L
Toluene	0.33 mg/L
TDS	500 mg/L
TSS	45 mg/L
Uranium	30 µg/L
Zinc	65 µg/L

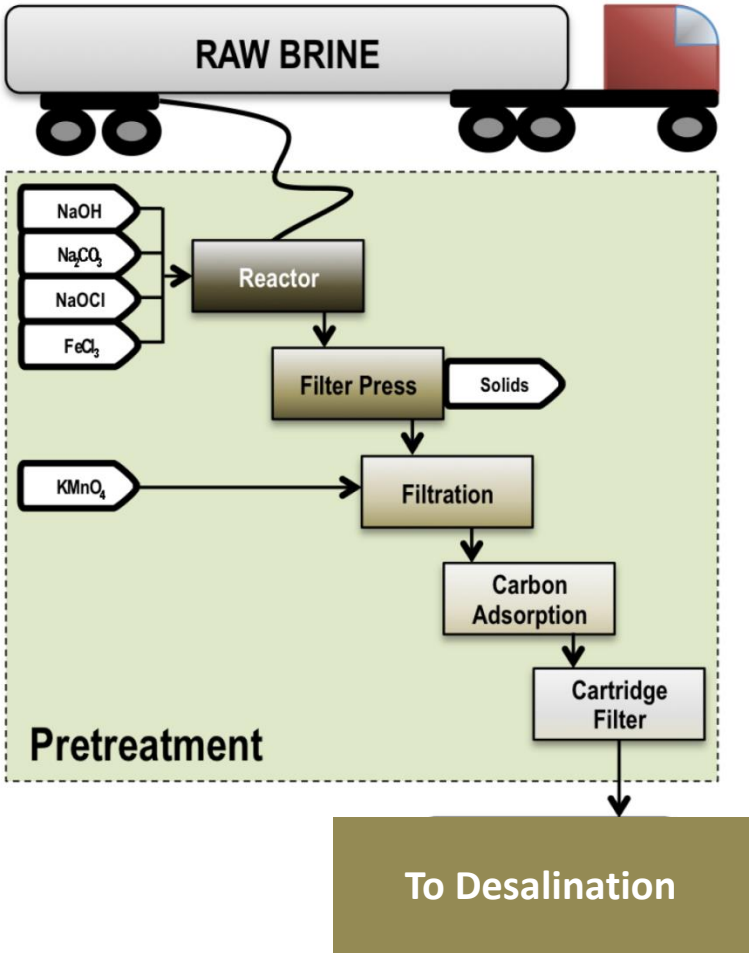
PA DEP Permit: WMGR 123

TX: Toughened SWD permitting and water availability for re-use

- Increased drilling operations and enhanced need for water
- Lack of fresh-water availability in desert environments, e.g. Permian
- Environmental concern and longer permitting times, e.g. East Texas
- Recent ability to store desalinated water in un-permitted pits encourages recycling

Pre-treatment can be a significant part of end-to-end process

Pre-treatment for membrane-based desalination



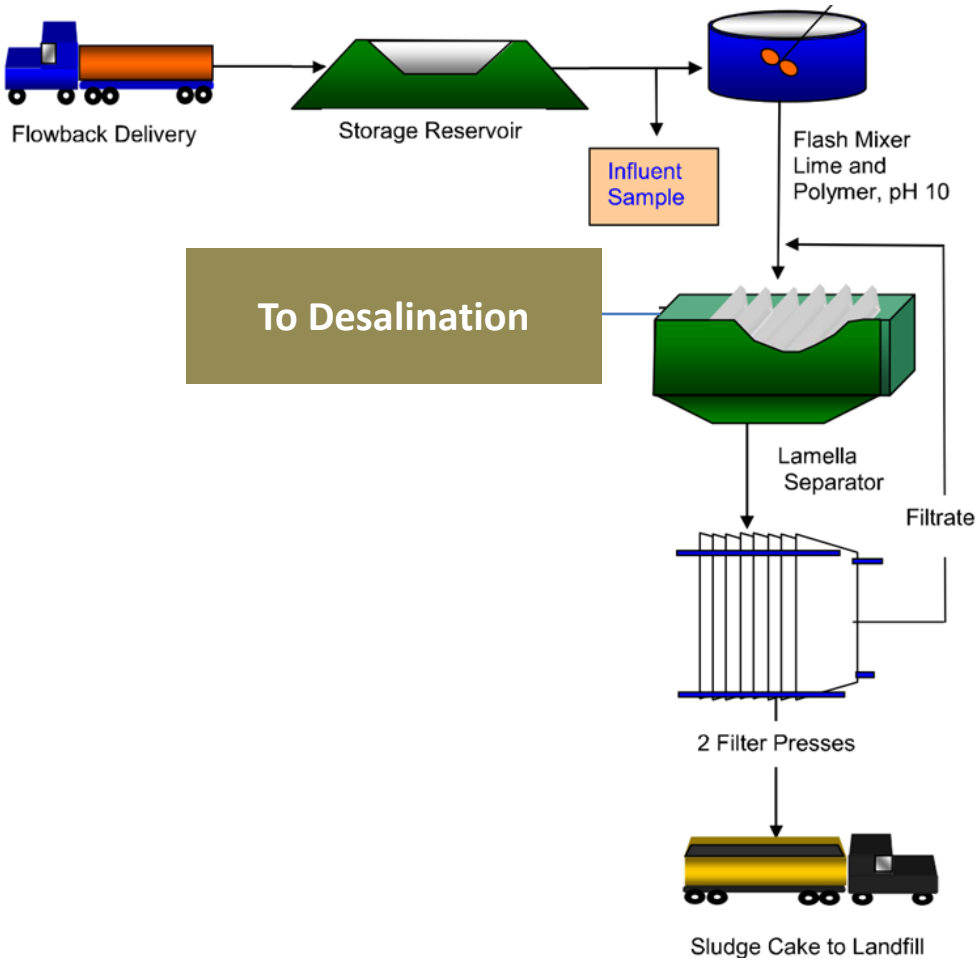
1. Removal of TSS (<10 mg/ L)
   Max. particle size 10 μm
1. Removal of suspended and emulsified O&G (<10 mg/L)
2. TOC removal
3. Removal of VOCs (where needed)
4. Scale prevention (removal of Ca^{2+}, Mg^{2+} etc.)

Source: McGinnis, Oasys Water

GRADIANT CORPORATION

Pre-treatment can be a significant part of end-to-end process

Lesser pre-treatment generally required for thermal desalination



Source: Fountain Quail Water Management (www.aqua-pure.com)

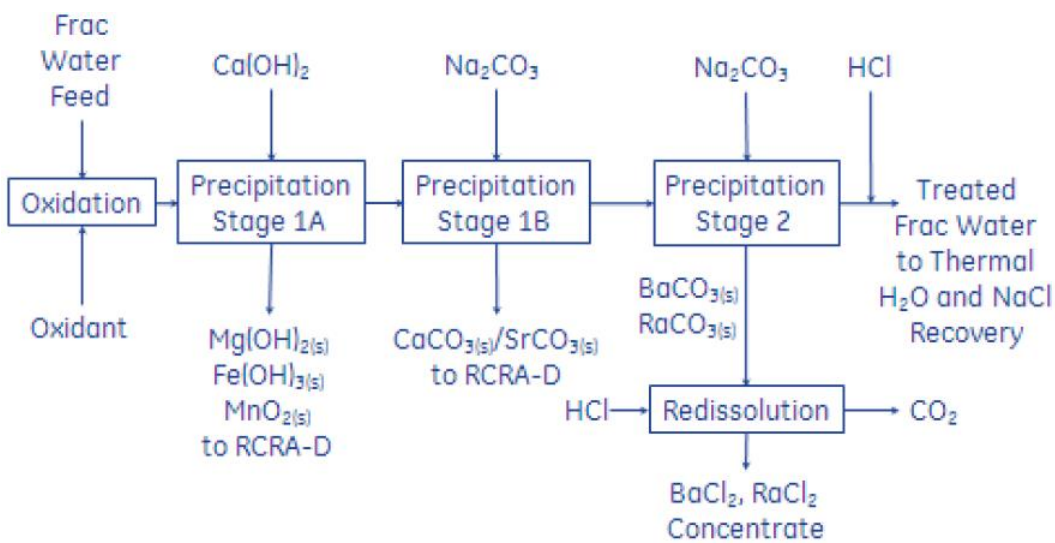
GRADIANT CORPORATION

Precipitation of NORM could add to waste disposal cost

Barium and Radium precipitate with Calcium and Magnesium

- This could make the pre-treatment waste radioactive

A modified soda-lime process is suggested to eliminate NORM in pre-treatment sludge



Species	Solubility, gm/100 gm H_2O	Temperature, °C
$MgCO_3.5H_2O$	0.176	7
$MgCO_3$	0.0106	~20
$CaCO_3$ (calcite)	0.0014	25
$CaCO_3$ (aragonite)	0.00153	25
$SrCO_3$	0.0011	18
BaCO3-alpha	0.002	20
$BaCO_3$-beta	0.022	18
$BaCO_3$-gamma	0.0022	18
$RaCO_3$	more soluble than barium carbonate[24]	

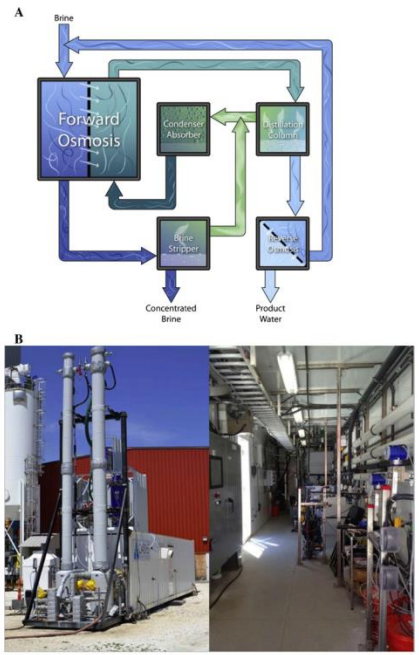
Source: General Electric Company

GRADIANT CORPORATION

Affordable, high TDS, high recovery desalination is an ideal solution

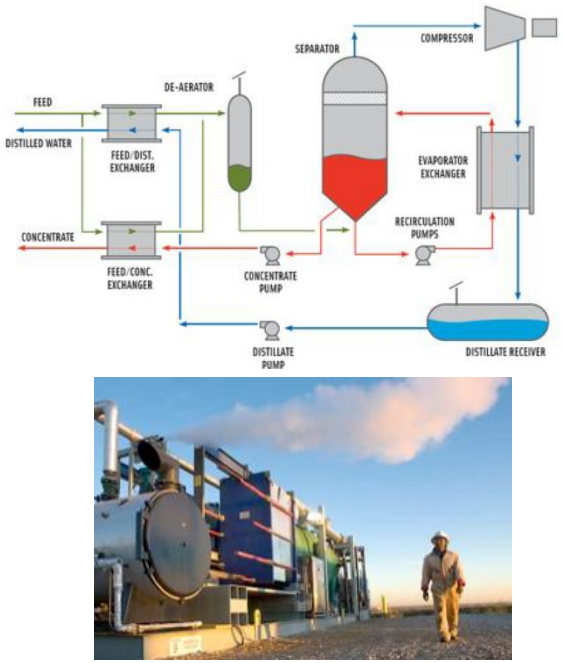
- Removal of TDS to discharge/ re-use levels (ideally <500 ppm)
- Solution must be able to handle salt saturation levels to achieve reasonable recovery
- Various technologies have been or are being tested:

Forward Osmosis



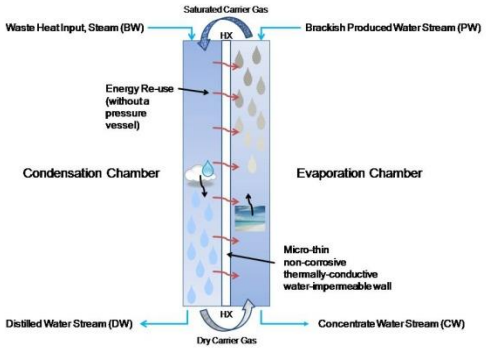
Source: McGinnis, Oasys Water

Mechanical vapor compression (MVC/ MVR)



Source: Fountain Quail

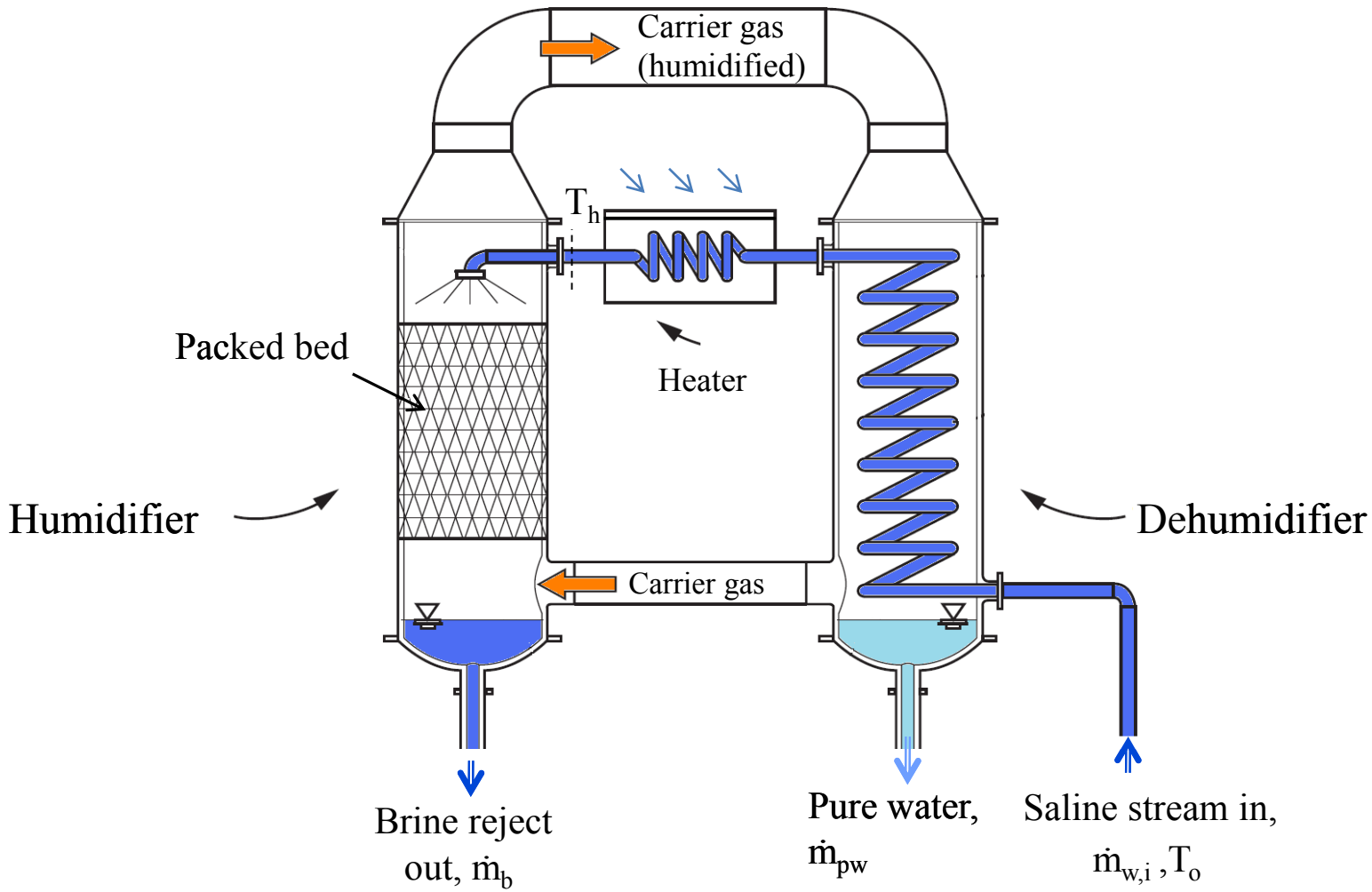
DewVaporation



Source: Altela, Inc.

GRADIANT CORPORATION

Gradiant's Carrier Gas Extraction (CGE™) for high recovery desalination of high TDS produced water



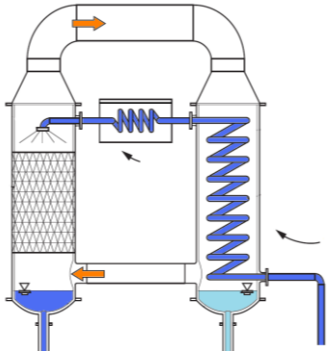
GRADIANT CORPORATION

CARRIER GAS EXTRACTION (CGE™)

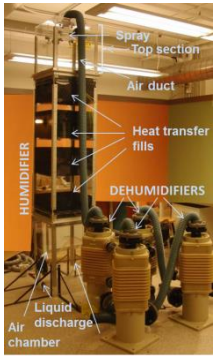
FOR ZERO LIQUID DISCHARGE (ZLD) DESALINATION

TECHNOLOGY DEVELOPMENT TIMELINE

Concept
MIT Sep '09



Lab system
MIT, Dec '11



10 bpd ZLD demo
Gradiant, Apr '13

50 bpd pilot
Gradiant, Aug '13

500 bpd ZLD field unit
Gradiant's site in Texas, Dec '13

PROGRESS SUMMARY

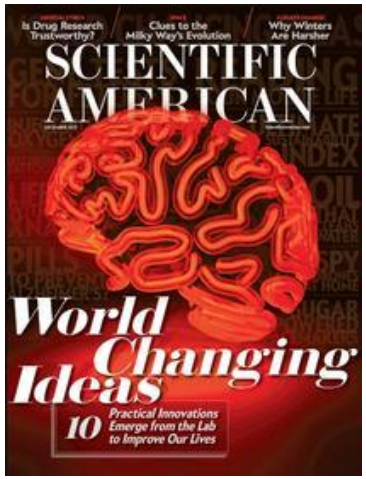
- **Working with industry partners Gradiant has successfully treated thousands of gallons of high TDS industrial brines**
- **Secured first commercial contract with large US E&P operator for treatment of oil & gas produced water**
- **Identified applications and established customer relationships in textile, tanning, and secondary seawater recovery**
- **CGE™ awarded the Water Technology Idol for 2013 by Global Water Intelligence**
- **IP portfolio of 21 filed patents (included 8 issued patents) developed or licensed exclusively at/by Gradiant**
- **Commercial site expansion to 4000 bpd in Q1 2014 and other projects in development**

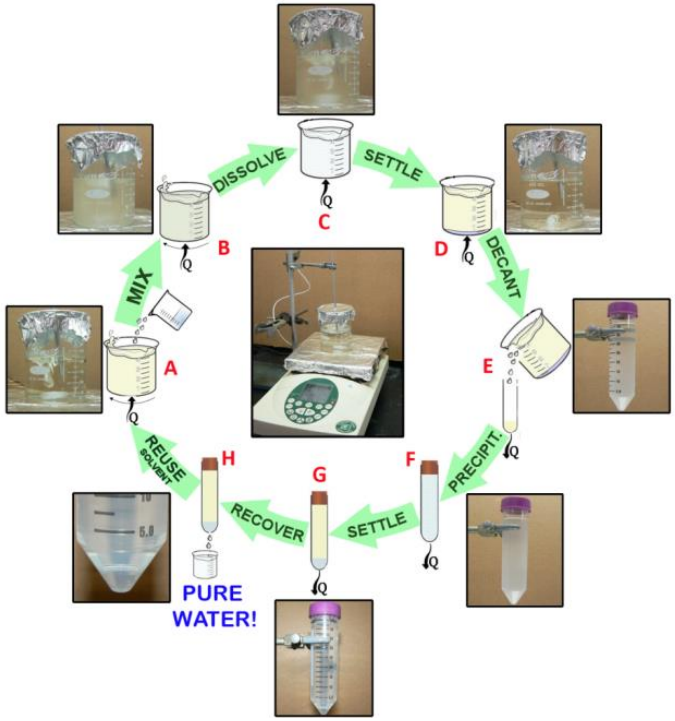
Carrier Gas Extraction (CGE™) plant is now in field operation

- **Commercial demonstration completed today in the Permian basin – further announcement in a week**
- **Ramping up to interim scale of 4000 bpd**
- **Scalable, modular design allows for varying throughput rates**
- **No membranes, ambient pressure, mid-temperature operation allows for high brine concentrations**
- **Ability to go to zero liquid discharge by novel crystallization and high recoveries**

Gradiant continues active R&D on complimentary technologies

- **Directional Solvent Extraction (DSE) for small scale desalination**
  - Technology in early stage of development
  - Liquid carrier fluid reduces footprint opening up smaller scale possibilities
  - Recognized by Scientific American as Top 10 World Changing Idea





- **Ion caging pre-treatment technology to replace softening also under development**

GRADIANT CORPORATION

Produced water desalination: Takeaways

- Low cost, high TDS, high recovery desalination for oil and gas produced water is the holy grail of water treatment
- Produced water treatment represents one of the greatest challenges and opportunities of our time
- Pre-treatment for membrane desalination can be prohibitively expensive
- Thermal desalination energy consumption and capital cost can be very high
- There are still no accepted industry-standard technologies. CGE has the promise of becoming one.

govindan@gradiantcorp.com